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Examination about Fabricating Conditions and Photoluminescence Intensity of Silicon Fine Particles

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Abstract

We fabricated Si:SiO_2 films and assessed its optical characteristics using photoluminescence spectroscopy. Sputtering was our method of fabricating thin film including silicon fine particles. Argon gas was used as an electrical discharge gas for the sputtering, pressure of the gas was 0.5 Pa and 0.9 Pa. Silicon (Si) and silicon dioxide (SiO_2) were put on a sputtering target. Composition ratio of the Si for the target was during 0.04 and 0.16. Growth rate of thin film was 0.18 nm/s at 0.5 Pa and 0.10 nm/s at 0.9 Pa, which didn't depend on the composition ratio. For the photoluminescence spectra of the Si:SiO_2 films fabricated, emission intensity was higher in the shorter than 450 nm region. And such intensity for 0.9 Pa was higher than it for 0.5 Pa, was higher at low composition ratio. A rising at 420 nm for 0.5 Pa spectra, was discussed in a view of quantum confinement effect.

Keywords

Si:SiO_2 Films; Silicon; Fine Particles; Co-sputtering; Photoluminescence

Introduction

By the spread of the internet and the change of the lifestyle, high function and many functionalization advances, mobile devices including a cell-phone are remarkably developing. The higher performance of the mobile devices is furthermore required. Among the performance, a display equipped with the device demands a big screen, high accuracy, thin and narrow frame, etc. In recent years, it has also succeeded in generation of nanosize silicon crystal which is full color and emits light in an ultraviolet range, and near-ultraviolet and luminescence in the purple [1]. And three primary colors of light are also checked from spectroscope measurement of the nanosize silicon crystal. Silicon materials, such as Amorphous-Si, Poly-Si, porous-Si and Si-fine particles are also expected as new element of display [2, 3].

In order to use the silicon materials for display, source and mechanism of luminous emission need to be solved. It is thought quantum confinement effects, localized states at the surface of nanosaize particles, and silicon-based luminous compounds such as siloxene and polysilane, etc. [3] as the emitting source. Since the emission was observed from the Si-fine particles using photoluminescence (PL) spectroscopy, lots of studies have been carried out [4, 5]. In order to improve photoluminescence intensity, doping of Er etc. has also been reported [6]. However the mechanism of the PL is still under debate [7]. We fabricated Si:SiO_2 films containing nanosized Si particles in uniform as fine particles by a radio frequency (rf) sputter device and analyzed optical characteristics by the PL spectroscopy. The relation between pressure of the argon (Ar) gas and composition ratio in the sputtering and the intensity of the photoluminescence were summarized in this paper.

Methods

The Si:SiO_2 nanosize films were fabricated by the rf sputter device. When these films were excited by irradiating of a He-Cd laser beam, the PL emission spectra from the Si:SiO_2 films were measured with a polychromator from 350 nm to 650 nm at room temperature.

Fabrication Methods

The Si:SiO_2 nanosize films were fabricated using the co-sputtering method of Si and SiO_2 [8]. Six Si tablets (15 mm

square) were placed on a SiO_2 plate (diameter 108 mm) as a target in the chamber of the rf sputter device. The composition ratio of Si to SiO_2 gradually changed from 0.04 to 0.16. The rf sputtering was started after the chamber was evacuated below 5.0×10^{-4} Pa as base pressure. As the sputtering conditions, the pressure of the Ar gas was set at 0.5 Pa or 0.9 Pa, and the rf power was fixed on 100 W. In this chamber, ionized Ar gas was made to collide with the target, the Si and SiO_2 were sputtered. When the Si:SiO_2 films were fabricated, it is thought that Si-fine particles surrounded by SiO_2 were accumulated on the Si substrate. Film thickness was supervised with a thickness meter of crystal oscillator during fabrication so that it was set to 600 nm.

Measurements Method

To investigate the light emission from the Si:SiO_2 films the PL was measured with a polychromator from 350 nm to 650 nm at room temperature [9]. When the films were excited by vertical irradiation of a He-Cd laser beam, wavelength 325 nm, (Kimmon, IK3251R-F) the PL was emitted. It was detected by a sensor probe of this polychrometer, which has CCD linear image sensor as photosensitive device. Number of channels in this image-sensor is 1024. In order to prevent the laser beam going into the sensor probe, the incidence angle was enlarged. Moreover, photoluminescence spectra were measured and these intensity was compared about the various conditions of fabrication. .

Results

After the fabrication, the thickness of the Si:SiO_2 films was measured by a surface-texture measuring instrument. The PL was emitted as the result of the irradiating by the He-Cd laser. Spectra of the PL were measured by the polyclometer.

Film thickness

The Si:SiO_2 films were fabricated under various conditions on the gas pressure and the composition ratio using the sputter device. Thickness of the films were about 600 nm by the surface-texture measuring instrument. As the film thickness and sputtering deposition time are considered, growth rate is calculated. This sputtering deposition time is about 100 minutes for 0.9 Pa of the Ar gas pressure and about 60 minutes for 0.5 Pa. The growth rates are compared at 0.5 Pa and 0.9 Pa, as shown in Fig. 1. This rate is 0.10 nm/s for the rate 0.04, 0.07 and 0.16, and 0.11 for the rate 0.10 and 0.12 for 0.9 Pa. These values are almost constant and does not depend on the composition ratio between 0.04 and 0.16. For 0.5 Pa, growth rate is 0.18 nm/s at 0.04, 0.17 nm/s at 0.07 and 0.19 nm/s at 0.16. Average of these growth rate is about 0.18 nm/s between 0.04 and 0.10. Since the growth rate does not change much even if the composition ratio of Si is changed, it is guessed that the mass of the Si or SiO_2 particles splattered by this sputtering is almost the same. Under the same pressure, because the kinetic energy of the Ar cations and the impact on the target is depending on the rf sputtering power, the mass of the splattered particles might be the same. As compared about the deposition time, it of the 0.5 Pa is 1.8 times faster than it of the 0.9 Pa. When the Ar gas pressure is higher the film is fabricated inefficiently. In this case, Ar pressure and growth rate are a inverse relation. It might be that particles of Si and SiO_2 generated by the collision of Ar cations in the gas are barred by other Ar cations and these do not reach the Si substrate. Shorter free path at 0.9 Pa might be a cause of the low growth rate.

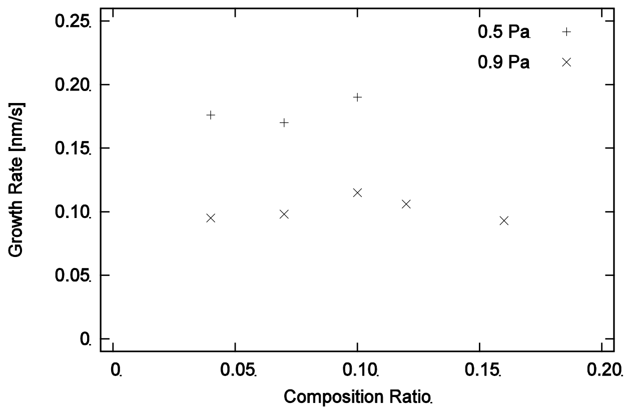

FIG. 1 GROWTH RATE DEPENDED ON COMPOSITION RATIO

Photoluminescence

PL spectra of the $Si:SiO_2$ films fabricated at 0.9 Pa were measured by the polychrometer. As the composition ratio of Si to the target varied from 0.04 to 0.16, five PL spectra are shown as a function of wavelength between 350 nm and 650 nm in Fig. 2. The bluish color emission was seen by the naked eye at room temperature. The emission intensity becomes more higher in ultraviolet region. As the wavelength was longer from 350 nm, it rapidly decreases. The peak is not observed on these spectra.

The PL is emitted strongly at low composition ratio of Si. As the composition ratio increases, the emission decreases. At 350 nm the emission intensity of ratio 0.07 is 1/2 times against it of 0.04. In the same way, it is 1/3 times for 0.10, and is about 1/5 times for 0.12 and 0.16. Emission can be hardly seen with naked eyes for the 0.16. Trend of these spectra does not change in 400 nm and 450 nm. In the region longer than 500 nm, the intensity is very weak and it does not distinguish each other.

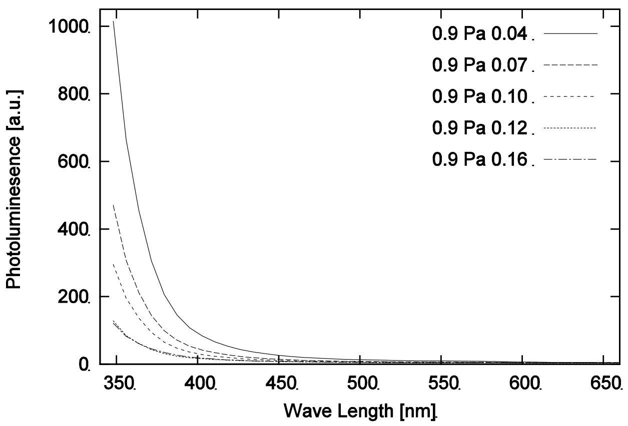

FIG. 2 PHOTOLUMINESCENCE OF THE $Si:SiO_2$ FILMS

If this PL emission is due to nanometer-sized quantum effect, it can be imaged that the Si-fine particles are surround with the SiO_2 and are isolated with each other [10, 11]. If it is assumed that the emission peak is present in the shorter than 350nm region, the diameter of these fine particles is calculated to be less than 5 nm using this quantum effect [12]. If the composition ratio of Si increases, the amount of SiO_2 relatively decreases. The reason for the phenomenon of the decreasing of emission intensity with Si composition ratio might be that the quantum confine effect does not work well with the decreasing of the SiO_2.

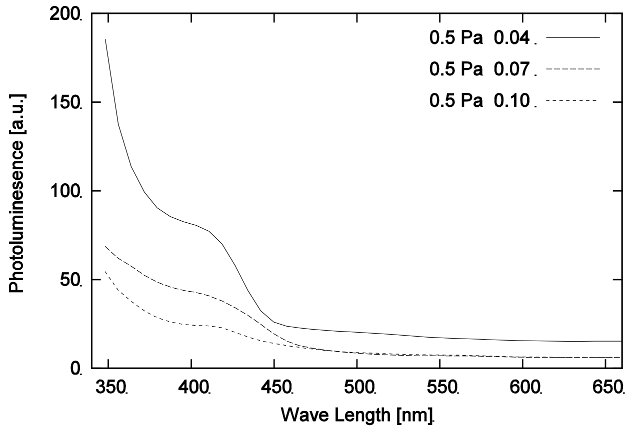

FIG. 3 PHOTOLUMINESCENCE OF THE $Si:SiO_2$ FILMS

PL spectra of the $Si:SiO_2$ films fabricated at 0.5 Pa of Ar gas are shown between 350 nm and 650 nm in Fig. 3. There are three spectra corresponding to different composition ratio. These emission also were seen in bluish color at room temperature. The emission intensity is higher in the short wavelength region. As the wavelength becomes longer, the intensity steeply weakened from 350 nm to 450 nm. But it is not changed over 450 nm. The peak is not observed, but a rising is seen at 420 nm (3.0 eV) for three spectra. Wavelength of the rising is constant even if the composition ratio is changed. If the quantum effect is a cause of the rising, the diameter is calculated about 6 nm.

This PL is emitted strongly at low composition ratio of Si. As this ratio increases the emission decreases. At 350 nm, intensity of the PL for this ratio 0.04 is 2.5 times it of 0.07, 3.5 times it of 0.10. Changes due to the composition ratio are similar to 0.9 Pa.

For comparison of differences of the Ar gas pressure, two spectra that have lowest composition ratio, 0.04, are compared in Fig. 4. Both spectra have high intensity at 450nm or less. Emission intensity of the filmes fabricated at 0.5 Pa is higher than that of the 0.9 Pa less than 400 nm. But between 400 nm and 450 nm, that of the 0.5 Pa is higher than one of the 0.9 Pa and the rising is seen at 420 nm. If this rising is recognized as a peak, full width of half maximum is 0.22 eV. These become about the same intensity at 450nm. Both spectra become flat at the region where the wavelength is longer than 450 nm, and that of the 0.5 Pa becomes high again.

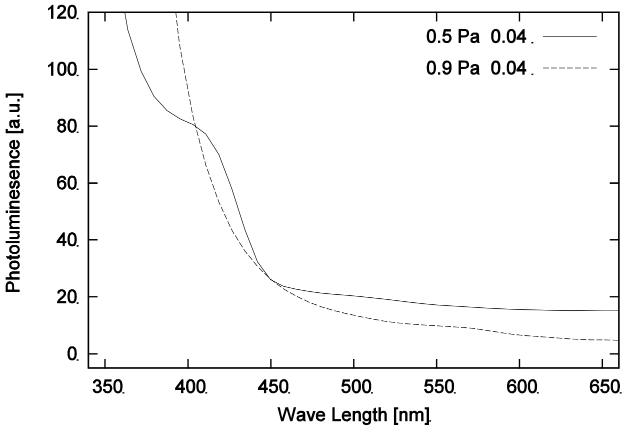

FIG. 4 PHOTOLUMINESCENCE OF THE $Si:SiO_2$ FILMS

At 0.9 Pa of the Ar pressure, it is considered that a peak might be at a wavelength shorter than 350 nm and that the size of the fine particles is smaller. Also, assuming that a region around 400 nm spectrum is a base of a large and wide peak, the size might have variety. Based on amplitude relation of the above two spectra, emission wavelength of the film fabricated at 0.5 Pa is likely longer than those at 0.9 Pa. The rf power is the same as 100 W about both Ar pressure. Because Ar cation has longer mean free path at 0.5 Pa and can collide with the target with greater kinetic energy, mass and diameter of sputtered Si or SiO_2 particles might be large. This is consistent with the faster growth rate in 0.5 Pa.

Since the three spectra for 0.5 Pa have the rising, emission intensities at 420 nm about the PL of the all films fabricated at 0.5 Pa and 0.9 Pa are plotted as a function of the composition ratio in Fig. 5. Intensity for 0.5 Pa is higher than that of 0.9 Pa. The emission intensity of lowest composition ratio, 0.04, is higher than those of other large composition, which is 1.5 times it of 0.07 and three times it of 0.10. When the composition ratio increases, the emission intensity decreases. Even if the gas pressure changes, the tendency doesn't change. About the 0.9 Pa spectra, the intensity of 0.04 is 1.5 times it of 0.07, three times it of 0.10, four times it of 0.12 and four times it of 0.16. The intensity didn't change so much between 0.12 and 0.16. The intensity difference between 0.5 Pa and 0.9 Pa at 0.04 is large, the difference in 0.10 is reduced. However, intensity ratio of 0.5 Pa to 0.9 Pa doesn't change so much in 1.2.

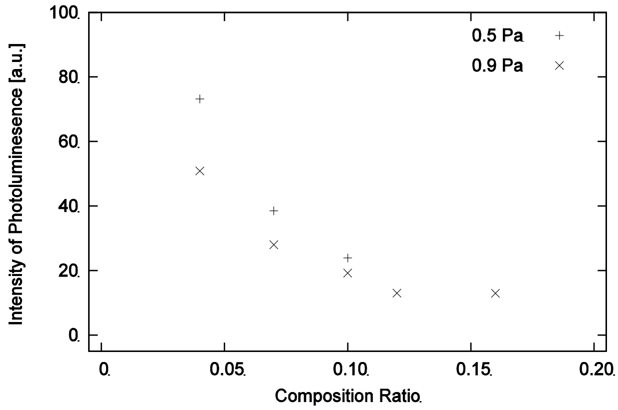

FIG. 5 INTENSITY OF PHOTOLUMINESCENCE AT 420 nm

About the films fabricated at 0.5 Pa and 0.9 Pa, all emission intensities on 350 nm are plotted as a function of the composition ratio in Fig. 6. The emission intensity of 0.04 which is the lowest composition ratio is higher than other large compositions. As opposed to 420 nm, emission intensity of the 0.9 Pa spectra is higher than that of the 0.5 Pa spectra. About the 0.9 Pa spectra, intensity of 0.04 is at least 2 times it of 0.07, three times it of 0.10, eight times it of 0.12 and eight times it of 0.16. The intensity didn't change so much between 0.12 and 0.16. Even if the Ar pressure changes, the tendency doesn't change. About 0.5 Pa, intensity of 0.04 is 2.5 times it of 0.07, 3.5 times it of 0.10. The intensity difference between 0.5 Pa and 0.9 Pa at 0.04 is large, the difference in 0.10 is reduced. However, intensity ratio of 0.5 Pa to 0.9 Pa does not change much at about 5.2 times.

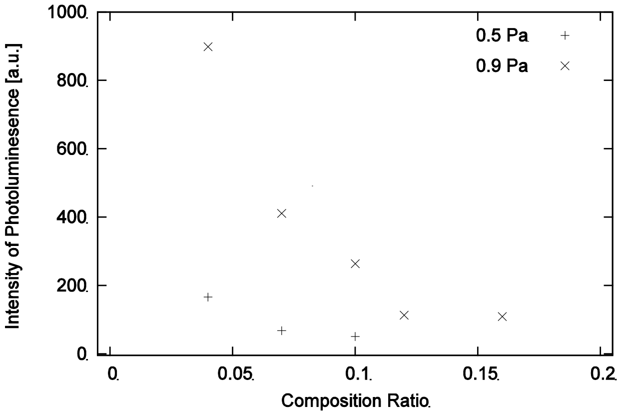

FIG. 6 INTENSITY OF PHOTOLUMINESCENCE AT 350 nm

The emission intensity of the film fabricated in the 0.9 Pa is higher than that in the 0.5 Pa. When the thickness and the composition ratio of these films are equal, if the diameter of the fine particles in the film is different, it is considered that number of Si-fine particles of 0.9 Pa is large. This large number might have caused the emission intensity. If it has an assumption that Si-fine particles are formed, for which quantum confined effect occurs in the thin film, these phenomena are well explained.

Conclusion

We have fabricated the $Si:SiO_2$ thin films by varying the composition ratios of Si 0.04 to 0.16 at the Ar gas pressure of 0.9 Pa and 0.5 Pa, using the co-sputtering method. The growth rates of the film setting to 600 nm were 0.10 m/s for 0.9 Pa and 0.18 m/s for 0.5 Pa. The emission intensity of the photoluminescence spectra was higher in 450 nm or less, was higher at the low composition ratio. And this intensity for 0.9 Pa was higher than that for 0.5 Pa. The rising was seen at 420 nm for 0.5 Pa spectra. If it had an assumption that the quantum confined effect occurs in these thin films, these phenomena were well explained. The size of the Si-fine particles that was calculated by this effects was less than 6 nm.

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REFERENCES

[1] Gelloza, B., R. Mentek, N. Koshida, "Ultraviolet and Long-Lived Blue Luminescence of Oxidized Nano-Porous Silicon and Pure Nano-Porous Glass", Journal of Solid State Science and Technology, 3, (2014) , pp. 83-85.

[2] Ito, M., C. Miyazaki, M. Ishizaki, M. Kon, N. Ikeda, T. Okubo, R. Matsubara, K. Hatta, Y. Ugajin, N. Sekine, "Application of amorphous oxide TFT to electrophoretic display," Journal of Non-Crystalline Solids, 354, (2008) pp. 2777–2782.

[3] Banihashemian, Seyedeh Maryam, Hassan Hajghassem, Alireza Erfanian, Majidreza Aliahmadi, Mansor Mohtashamifar and Seyed Mohamadhosein Mosakazemi "Observation and Measurement of Negative Differential Resistance on PtSi Schottky Junctions on Porous Silicon," The Journal of Sensors, 10, (2010) 1012-1020; doi:10.3390/s100201012.

[4] Canham, L. T., "Silicon quantum wire array fabrication by electrochemical and chemical dissolution of wafers", Appl. Phys. Lett., 57, (1990) pp. 1046-1048.

[5] Biteen, Julie S., Nathan S. Lewis, and Harry A. Atwater, Hans Mertens and Albert Polman, "Spectral tuning of plasmon-enhanced silicon quantum dot luminescence", Appl. Phys. Lett., 88, (2006) 131109.

[6] Isshiki, H., M. J. A. de Dood and A. Polman, T. Kimura, "Self-assembled infrared-luminescent Er–Si–O crystallites on silicon", Appl. Phys. Lett., 85, (2004), pp. 4343-4345.

[7] Yamada, Y., T. Orii, I. Umezu, S. Takeyama, and T. Yoshida, "Optical Properties of Silicon Fine particles Prepared by Excimer Laser Ablation in Inert Gas", Jpn. J. Appl. Phys., 35, (1996), pp. 1361-1365.

[8] Hanaizumi, O., G. Saito, Y. Ohtera, S. Kawakami, S. Yano, Y. Segawa, E. Kuramochi, T. Tamamura, S. Oku, A. Ozawa, "Fabrication and Assessment of Sputtered Si:SiO_2 Films Emitting White Light without Annealing", Jpn. J. Appl. Phys., 41, (2002), pp. L1084-L1087.

[9] Tanaka, K., N. Happo and M. Fujiwara: Proc. of Inter. Semiconductor Conference (CAS), Vol. 1, (2012), p.171.

[10] Brandt, M. S., H. D. Fuchs, M. Stutzmann, J Weber, and M. Cardona, "The origin of visible luminescencefrom 'porous silicon': A new interpretation", Solid States Commun., 81, (1992), pp. 307–312.

[11] Boukherroub, R., Danial D. M. Wayner and David J. Lockwood, "Photoluminesence stabilization of anodically-oxidized porous silicon layers by chemical functionalization", Appl. Phys. Lett., 81, (2002), pp. 601-603.

[12] Zhu, Weijuan, Xiaohong Yan, Yang Xiaoe, "Hexagonal silicon nanotube confined inside a carbon nanotube: A first-principles study", Physics Letters A, 372, (2008), pp. 1308–1312.

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